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## PATENT SPECIFICATION

(11) 1 518 495

(21) Application No. 19786/77 (22) Filed 11 May 1977

(31) Convention Application No. 2 621 657

(32) Filed 15 May 1976 in

(33) Fed. Rep. of Germany (DE)

(44) Complete Specification published 19 July 1978

(51) INT CL<sup>7</sup> C08L 67/02 (C08L 67/02, 61/20)

(52) Index at acceptance

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C6B C8R L1A L1B L2X L5D L5X L6G

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MANFRED PATHEIGER

## ERRATUM

SPECIFICATION No. 1,518,495

Page 1, Heading (72), Inventors, for WOL-  
GANG read WOLFGANGTHE PATENT OFFICE  
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mentioned property is especially desirable in the case of those coating agents which are processed by the so-called coil coat technique (that is to say lacquer coating of a continuous web of sheet metal, which is shaped only after coating has been effected).

The coating agents according to the invention can be applied in high concentration and thus reduce the lacquer costs, the contamination of places of work by solvent vapours and the amounts of energy and time required for curing the lacquer.

Stoving lacquers which are low in solvent or free from solvent are based on aminoplasts + polyester are already known. Thus, German Offenlegungsschrift (German Published Specification) 1,644,848 provides solvent-free coating agents based on fatty acid-free polyesters and specific aminoplasts. The coatings produced in accordance with the example in this publication exhibit good mechanical properties but these deteriorate markedly after pigmentation.

Coating agents which are low in solvent

coil-coat coatings are combined.

Surprisingly, it has now been found that coating agents which give lacquer coatings with very good mechanical properties, exceptionally good weathering characteristics and outstanding adhesion to sheet metal are accessible by a very specific choice of the individual polyester components, the molar ratios of these components and the molecular weight of the polyester to be prepared.

The present invention provides a coating agent comprising an organic solvent and a binder composition comprising a mixture of a first binder component and a second binder component in the ratio of from 5 to 30: 95 to 70 wherein the first binder component is an aminoplast and the second binder component is a linear polyester which contains hydroxyl groups and carboxyl groups, has a molecular weight of from 2500 to 5000, and is obtainable by the polycondensation of:

a first condensation component comprising from 9 to 20 mol % of hexane-1,6-diol and from 91 to 80 mol % of an alkanediol component which comprises (1.) from 69.9

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C6B C8R L1A L1B L2X L5D L5X L6G

(72) Inventors PETER HÖBLEIN, WOLFGANG BEER and

MANFRED PATHEIGER

(54) COATING AGENT FOR THE PRODUCTION OF COATINGS  
WHICH ARE RESISTANT TO WEATHERING

(71) We, BAYER AKTIEN-GESELLSCHAFT, a Company organised under the laws of Germany, of 509 Leverkusen, Bayerwerk, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to coating agents which, after stoving, give high-gloss coatings of great hardness and high elasticity, which are distinguished by such an excellent adhesion to sheet metal that they are able to withstand even extreme deformations of the substrate. The last-mentioned property is especially desirable in the case of those coating agents which are processed by the so-called coil coat technique (that is to say lacquer coating of a continuous web of sheet metal, which is shaped only after coating has been effected).

The coating agents according to the invention can be applied in high concentration and thus reduce the lacquer costs, the contamination of places of work by solvent vapours and the amounts of energy and time required for curing the lacquer.

Stoving lacquers which are low in solvent or free from solvent are already based on aminoplasts + polyester are already known. Thus, German Offenlegungsschrift (German Published Specification) 1,644,848 provides solvent-free coating agents based on fatty acid-free polyesters and specific aminoplasts. The coatings produced in accordance with the example in this publication exhibit good mechanical properties but these deteriorate markedly after pigmentation.

Coating agents which are low in solvent

or are solvent-free and are based on aminoplasts and linear polyesters of at least two dicarboxylic acids and at least two glycols are known from German Auslegeschrift (German Published Specification) 1,805,182 and the glycol component employed is an ethylene glycol/propane-1,2-diol mixture. These coating agents are suitable for the production of high quality transparent coatings; however, with a pigment content the good properties deteriorate greatly and then no longer meet the requirements in practice.

An object of the invention is to provide coating agents which are substantially free from the said disadvantages and in which the advantageous properties necessary for coil-coat coatings are combined.

Surprisingly, it has now been found that coating agents which give lacquer coatings with very good mechanical properties, exceptionally good weathering characteristics and outstanding adhesion to sheet metal are accessible by a very specific choice of the individual polyester components, the molar ratios of these components and the molecular weight of the polyester to be prepared.

The present invention provides a coating agent comprising an organic solvent and a binder composition comprising a mixture of a first binder component and a second binder component in the ratio of from 5 to 30: 95 to 70 wherein the first binder component is an aminoplast and the second binder component is a linear polyester which contains hydroxyl groups and carboxyl groups, has a molecular weight of from 2500 to 5000, and is obtainable by the polycondensation of:

a first condensation component comprising from 9 to 20 mol % of hexane-1,6-diol and from 91 to 80 mol % of an alkanediol component which comprises (1.) from 69.9

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to 20 mol % of ethylene glycol and (2.) from 30.1 to 80 mol % of a diol component comprising from 50 to 100 mol % of neopentyl glycol and from 50 to 0 mol % of 2-ethylpropane -1,3-diol, with a second condensation component comprising (1.) from 88 to 100 mol % of a phthalic component comprising from 65 to 100 mol % of phthalic acid or its anhydride and from 35 to 0 mol % of isophthalic and/or terephthalic acid and/or an anhydride thereof, and (2.) from 12 to 0 mol % of one or more of cycloaliphatic dicarboxylic acids having from 8 to 12 carbon atoms and/or saturated aliphatic dicarboxylic acids having from 5 to 12 carbon atoms.

In another aspect the present invention provides a binder composition as defined hereinabove with reference to the coating agent of the present invention.

In further aspects the present invention provides a method of coating a metal surface comprising applying a coating agent according to the present invention to said metal surface, and stoving the coated metal surface and a coated metal surface produced by said method.

Preferably the polyesters employed are linear polyesters having a molecular weight of from 3,000 to 4,000. The composition of the first condensation component is preferably from 15 to 20 mol % of hexane-1,6-diol and from 85 to 80 mol % of the alkanediol component, which most preferably comprises from 30 to 50 mol % of ethylene glycol and from 70 to 50 mol % of the diol component.

Cycloaliphatic and saturated aliphatic dicarboxylic acids which can be used are, for example, cyclohexanedicarboxylic acids, glutaric acid, adipic acid, suberic acid, sebacic acid or decanedicarboxylic acid.

The average molecular weight is determined as a number-average by means of gel chromatography in tetrahydrofuran using a standard curve.

The polyesters can be prepared in a manner which is in itself known by a condensation reaction according to customary processes. In general, the mixtures of raw materials are allowed to react at temperatures of from 140 to 250°C in an inert atmosphere, for example under nitrogen, with the elimination of water until the desired molecular weight (or the corresponding viscosity or acid number, which are easier to determine) is reached.

Suitable aminoplast resins include, for example, melamine-formaldehyde condensation products or urea-formaldehyde condensation products. Melamine resins are all of the conventional melamine-formaldehyde condensation products which are optionally etherified with saturated

monoalcohols with 1 to 4 C atoms, such as those described, for example, in French Patent Specification 943,411 or in D. H. Solomon, *The Chemistry of Organic Filmformers*, 235-240, John Wiley & Sons, Inc., New York, 1967. The melamine resins can, however, also be wholly or partly replaced by other crosslinking aminoplasts, such as those described, for example, in "Methoden der Organischen Chemie" ("Methods of Organic Chemistry") (Houben-Weyl), Volume 14/2, part 2, 4th edition, George Thieme Verlag, Stuttgart, 1963, 319 et seq.

When preparing the polyesters, attention must be paid to the fact that both the molecular weight and the composition of the polyester influence the properties of the coatings produced from the coating agents according to the invention. As a rule, an increase in the molecular weight is coupled with an increase in the elasticity with, at the same time, a decrease in the hardness. The composition of the polyester also has a similar effect: whilst the elasticity increases and the hardness of the coatings decreases with a higher proportion of aliphatic dicarboxylic acids and with a longer chain length of the aliphatic dicarboxylic acids, the coatings containing an increasing proportion of aromatic and/or cycloaliphatic dicarboxylic acids are, conversely, harder and less elastic. An increase in the proportion of isophthalic acid or terephthalic acid leads to greater hardness and lower resistance to weathering, whilst an increase in the hexane-1,6-diol content has an adverse effect on the hardness.

In connection with the weight ratio polyester/aminoplast, it must be taken into account that the hardness of the coatings increases and their elasticity is reduced as the proportion of aminoplast increases. These rules make it possible, without difficulty, to produce, within the scope of the claimed range, coatings which have precisely the desired properties.

Organic solvents which are suitable for the coating agents according to the invention are the customary lacquer solvents, such as, for example, alcohols with 1-4C atoms, such as methanol, ethanol, n-propanol, isopropanol and the butanols; acetic acid esters with 2-4C atoms in the alcohol component, such as ethyl acetate and butyl acetate, or ethyl glycol acetate; ethylene glycol monoalkyl ether with 1-4C atoms in the alkyl radical, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and ethylene glycol monobutyl ether; aliphatic and alicyclic ketones, such as methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone and acetone; lower ethers, such as tetrahydrofuran; chlorinated hydrocarbons, such as tri-

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chloroethylene; and aromatic hydrocarbons, such as benzene, toluene, and xylene, or mixtures of the said solvents. As a rule, the solvent is employed in an amount of from 5 to 35% by weight of the resulting solution.

The coating agents according to the invention can contain customary auxiliaries, for example pigments, flow control agents or fillers. The lacquer films, which are usually applied in a layer thickness of 20  $\mu$  to 30  $\mu$ , can be stored at temperatures of from 180 to 340°C.

As is known, the through-curing of polyester/aminoplast binders is accelerated by the addition of an acid. When polyesters with a very low acid number are used, acid catalysts can be added to the coating agents according to the invention. Thus, for example, through-curing is greatly accelerated when 0.5% by weight, relative to the sum of the components A and B, of p-toluenesulphonic acid is added.

It is also possible to add about 1 to 5% by weight, relative to polyester, of an anhydride of a dicarboxylic acid which reduces the temperature at which the coating agent can be cured, for example maleic anhydride, to polyesters which have a low acid number in order subsequently to increase the acid number and thus to lower the storing temperatures even without the addition of acid catalysts.

Unless otherwise stated, the parts indicated in the examples which follow denote parts by weight.

#### EXAMPLE 1.

90 mol % of a phthalic component consisting of 2,079 parts of phthalic anhydride (77.8 mol % of the phthalic component) and 666 parts of isophthalic acid (22.2 mol % of the phthalic component); 293 parts of adipic acid (10 mol %); 622 parts of ethylene glycol (55.6 mol % based on the diols other than hexane diol-1,6), 835 parts of neopentyl glycol (44.4 mol % based on the diols other than hexane diol-1,6) and 474 parts of hexane-1,6-diol (18 mol % based on all of the diols) are heated under a nitrogen atmosphere, in a melt condensation apparatus, whilst slowly raising the temperature to 240°C in the course of 20 hours and the mixture is kept at this temperature until an acid number of less than 10 is reached. The resulting polyester is dissolved in a solvent mixture of ethylglycol acetate/benzene-toluene-xylene mixture (Solvesso 150, commercially available product from Messrs. Shell, Hamburg; Solvesso is a registered Trade Mark) (mixing ratio 1:1, relative to weight) to give a 65% strength by weight solution. The molecular weight of the polymer is 3640.

#### EXAMPLE 2.

Under the conditions according to Example 1, 999 parts of phthalic anhydride (70 mol % based on its combination with isophthalic and terephthalic acids present), 320 parts of isophthalic acid, 160 parts of terephthalic acid the combined isophthalic and terephthalic acids being present in a mol % of 30 in combination with the phthalic anhydride, 189 parts of ethylene glycol (31.1 mol % based on the diols other than hexane-1,6-diol), 351 parts of neopentyl glycol (34.5 mol % based on the diols other than hexane-1,6-diol), 351 parts of 2-ethylpropane-1,3-diol (34.5 mol % based on the diols other than hexane-1,6-diol) and 114 parts of hexane-1,6-diol (9 mol % based on all of the diols) are subjected to a polycondensation reaction and the reaction product is dissolved. The molecular weight of the polymer is 3280.

#### EXAMPLE 3.

Under the conditions according to Example 1, 95 mol % of a phthalic component consisting of 1,782 parts of phthalic anhydride (66.3 mol % of the phthalic component), and 1,000 parts of isophthalic acid (33.7 mol % of the phthalic component); 293 parts of adipic acid (the adipic acid being present in an amount of 10 mol % based on its combination with the phthalic component) 622 parts of ethylene glycol (55.6 mol % based on the diols other than hexane-1,6-diol), 835 parts of neopentyl glycol (44.4 mol % based on the diols other than hexane-1,6-diol) and 474 parts of hexane-1,6-diol (18 mol % based on all of the diols) are subjected to a polycondensation reaction and the reaction product is dissolved. The molecular weight of the polymer is 3820.

#### EXAMPLE 4.

Under the conditions according to Example 1, 90 mol % of a phthalic component consisting of 2,016 parts of phthalic anhydride (77.8 mol % of the phthalic component) and 646 parts of isophthalic acid (22.2 mol % of the phthalic component); 284 parts of adipic acid (the adipic acid being present in an amount of 10 mol % based on its combination with the phthalic component) 362 parts of ethylene glycol (30 mol % based on the diols other than hexane-1,6-diol), 708 parts of neopentyl glycol (35 mol % based on the diols other than hexane-1,6-diol), 708 parts of 2-ethylpropane-1,3-diol (35 mol % based on the diols other than hexane-1,6-diol) and 230 parts of hexane-1,6-diol (9 mol % based on all of the diols) are subjected to a polycondensation reaction and the reaction product is dissolved. The molecular weight of the polymer is 3470.



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**WHAT WE CLAIM IS:—**

1. A coating agent comprising an organic solvent and a binder composition comprising a mixture of a first binder component and a second binder component in the ratio of from 5 to 30:95 to 70 wherein the first binder component is an aminoplast and the second binder component is a linear polyester which contains hydroxyl groups and carboxyl groups, has a molecular weight of from 2500 to 5000, and is obtainable by the polycondensation of:
  - 15 a first condensation component comprising from 9 to 20 mol % of hexane-1,6-diol and from 91 to 80 mol % of an alkanediol component which comprises (1.) from 69.9 to 20 mol % of ethylene glycol and (2.) from 30.1 to 80 mol % of a diol component comprising from 50 to 100 mol % of neopentyl glycol and from 50 to 0 mol % 2-ethylpropane-1,3-diol, with a second condensation component comprising (1.) from 88 to 100 mol % of a phthalic component comprising from 65 to 100 mol % of phthalic acid or its anhydride and from 35 to 0 mol % of isophthalic and/or terephthalic acid and/or an anhydride thereof, and (2.) from 12 to 0 mol % of one or more of cycloaliphatic dicarboxylic acids having from 8 to 12 carbon atoms and/or saturated aliphatic dicarboxylic acids having from 5 to 12 carbon atoms.
  2. A coating agent as claimed in claim 1 wherein the organic solvent comprises from 5 to 35% by weight of the coating agent.
  3. A coating agent as claimed in claim 1 or claim 2 wherein the organic solvent comprises one or more of the customary solvents specifically mentioned hereinbefore.
  4. A coating agent as claimed in any of claims 1 to 3 which includes one or more of a pigment, a flow control agent and a filler.
  5. A coating agent as claimed in any of claims 1 to 4 which also includes an acid curing catalyst.
  6. A coating agent as claimed in claim 5 which contains up to 0.5% by weight relative to the binder composition of p-toluenesulphonic acid.
  7. A coating agent as claimed in any of the preceding claims which contains from 1 to 5% by weight, relative to the polyester, of an anhydride of a dicarboxylic acid so as to reduce the temperature at which the coating agent can be cured.
  8. A coating agent as claimed in claim 7 wherein the anhydride is maleic anhydride.
  9. A coating agent as claimed in any of the preceding claims wherein the linear

polyester has a molecular weight of from 3000 to 4000.

10. A coating agent as claimed in any of the preceding claims wherein the first condensation component comprises from 15 to 20 mol % of hexane-1,6-diol and from 85 to 80 mol % of the alkane-diol component.

11. A coating agent as claimed in any of the preceding claims wherein the alkanediol component comprises from 50 to 70 mol % of the diol component and from 30 to 50 mol % of ethylene glycol.

12. A coating agent as claimed in any of the preceding claims wherein said one or more cycloaliphatic and/or saturated aliphatic dicarboxylic acids comprises one or more of a cyclohexane dicarboxylic acid, glutaric acid, adipic acid, suberic acid, sebacic acid or decanedicarboxylic acid.

13. A coating agent as claimed in any of the preceding claims wherein the polycondensation is carried out at from 140 to 250°C in an inert atmosphere.

14. A coating agent as claimed in any of the preceding claims wherein the aminoplast is a melamine or ureaformaldehyde condensation product.

15. A coating agent as claimed in claim 14 wherein the melamine-formaldehyde condensation product is etherified with a saturated monoalcohol having from 1 to 4 carbon atoms.

16. A coating agent substantially as described hereinbefore with particular reference to Example 5.

17. A coating produced using a coating agent according to any of the preceding claims.

18. A method of coating a metal surface comprising applying a coating agent according to any of the preceding claims to said metal surface, and stoving the coated metal surface.

19. A method as claimed in claim 18 wherein the coating is applied in a layer having a thickness of from 20 $\mu$  to 30 $\mu$ .

20. A method as claimed in claim 18 or claim 19 wherein the stoving is effected at a temperature of from 180 to 340°C.

21. A method of coating a metal surface substantially as described herein with particular reference to Example 5.

22. A coated metal surface produced by a method according to any of claims 18 to 21.

23. A binder composition for use in a coating agent, which binder composition is as defined in claim 1.

24. A coating substantially as described hereinbefore with particular reference to Example 5.

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